Exhibit 1

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APPLICANT HENKEL CORPORATION

The patent office acknowledges, and has stamped hereon the date of the receipt of the items checked below:

( ) AFFIDAVIT OR DECLARATION
( ) AMENDMENT
( ) APPEAL NOTICE
( ) APPLICATION
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( ) DRAWINGS
( ) PCT TRANSMITTAL LETTER PTO-1390
( ) PETITION
( ) PRIORITY CLAIM
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( ) PCT TRANSMITTAL LETTER PTO-1382 (IF DUPLICATE)
( ) PCT REQUEST ___ PAGES; DESCRIPTION ___ PAGES; CLAIMS ___ PAGES; ABSTRACT ___ PAGES
( ) FEE CALCULATION SHEET (IN TRIPLICATE)
( ) RESPONSE TO INVITATION TO CORRECT DEFECTS
( ) POWER OF ATTORNEY
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- 1 CERTIFIED COPY OF JAPANESE PRIORITY DOCUMENT NO. H11-230060 FILED 16 AUGUST 1999

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Attention: RO/US

Re: PCT/US00/22335
International Filing Date: 16 August 2000
Priority Date Claimed: 16 August 1999
Applicant: Henkel Corporation
Title: PROCESS FOR FORMING A PHOSPHATE CONVERSION COATING ON METAL
Applicant's Reference: M 6741 HST/NI

TRANSMITTAL OF CERTIFIED COPY

Dear Sir or Madam:

Attached is one certified copy of the foreign application from which the priority is claimed for this case:

Country: Japan
Application Number: H11-230060
Filing Date:16 August 1999

Respectfully submitted,

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Encl.
(1) Japanese Priority Document
c: T. Niborski

日 本 国 特 許 庁
PATENT OFFICE
JAPANESE GOVERNMENT

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This is to certify that the annexed is a true copy of the following application as filed h this Office.

出願年月日 ate of Application:	１９９９年　８月１６日
願番号 plication Number:	平成１１年特許願第２３００６０号
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特許庁長官
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Patent Office

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出証番号　出証特２０００－３０７００１６

Exhibit 2

"Methods for the phosphate conversion treatment of metals"

Japanese Patent Application
Number Hei 11-230060 (230,060/1999)

Applicant: Nihon Parkerizing Co., Ltd.

Filing Date in Japan: 16 August 1999

Case M 6741 HST/NI

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Exhibit 2

(Document Designation)	Patent Application
(File Number)	99-19
(Application Date)	16 August 1999
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(Title of the Invention)	Methods for the phosphate conversion treatment of metals
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Title of the Invention

Methods for the phosphate conversion treatment of metals

Claims

Claim 1. Method for the phosphate conversion treatment of metals, that characteristically comprises

contacting a metal with a surface conditioning bath that contains phosphate particles having a diameter no greater than 5 μm and comprising at least 1 selection from phosphates that contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant component, at least 1 selection from monosaccharides, polysaccharides, and derivatives thereof, and

contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

Claim 2. Method for the phosphate conversion treatment of metals, that characteristically comprises

contacting a metal with a surface conditioning bath that contains phosphate particles having a diameter no greater than 5 μm and comprising at least 1 selection from phosphates that

contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant component, at least 1 selection from orthophosphoric acid, polyphosphoric acids, and organophosphonic acid compounds, and

contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

Claim 3. Method for the phosphate conversion treatment of metals, that characteristically comprises

contacting a metal with a surface conditioning bath that contains phosphate particles having a diameter no greater than 5 μm and comprising at least 1 selection from phosphates that contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant component, at least 1 water-soluble polymer compound selected from vinyl acetate polymers and derivatives thereof and the copolymers of vinyl acetate with monomer copolymerizable with vinyl acetate, and

contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

Claim 4. Method for the phosphate conversion treatment of metals, that characteristically comprises

contacting a metal with a surface conditioning bath that contains phosphate particles having a diameter no greater than 5 μm and comprising at least 1 selection from phosphates that

contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant component, at least 1 selection from the polymers and copolymers afforded by the polymerization of (a) at least 1 selection from monomers with chemical structure (1) and α,β-unsaturated carboxylic acid monomers and (b) no more than 50 weight% monomer copolymerizable with the aforesaid monomer (a)

(1) $H_2C{=}C(R^1){-}COOR^2$

(R^1 = H or CH_3, R^2 = H, C_1 to C_5 alkyl, or C_1 to C_5 hydroxyalkyl),

and contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

Claim 5. Method according to any of Claims 1 to 4 for the phosphate conversion treatment of metals, wherein the phosphate conversion treatment bath also contains from 0.1 to 3.0 g/L of at least 1 metal ion selected from the group consisting of the magnesium ion, cobalt ion, manganese ion, calcium ion, tungstate ion, and strontium ion.

(Detailed Description of the Invention)

(Field of the Invention)

This invention relates to methods for the phosphate conversion treatment of metals wherein said methods employ a nickel ion-free phosphate conversion treatment bath and produce a uniform, strongly paint-adherent, and highly post-painting corrosion-resistant coating on such metals as steel sheet, zinc-plated steel sheet, aluminum alloys, and magnesium alloys.

(0001)

(Description of the Prior Art)

Phosphate conversion treatments are currently executed as a pre-paint treatment on automotive body components in order to enhance corrosion resistance and improve the steel sheet-to-paint adherence. In these phosphate conversion treatments, the metal is first brought into contact with a colloidal titanium surface conditioning bath and is then brought into contact with an acidic solution containing phosphate ion, zinc ion, nickel ion, and manganese ion in order to precipitate a phosphate coating on the metal.

(0002)

However, in association with today's heightened concern with environmental protection, the regulatory situation with regard to nickel in wastewater has become increasingly stringent, particularly in Europe. It is certainly prudent to anticipate that regulations on nickel in wastewater might also become much more demanding in Japan in the future.

(0003)

These considerations make it desirable to eliminate the nickel from the conversion treatment baths used in zinc phosphate treatments.

(0004)

Unfortunately, a number of negative effects are caused by removal of the nickel from the phosphate treatment baths used in the aforementioned phosphate treatment processes: the crystals in the phosphate coating undergo coarsening, the phosphate coating suffers from a loss of uniformity, the post-painting corrosion resistance declines, and the secondary (water-resistant) adherence by the zinc-plated material also declines.

(0005)

Japanese Laid Open Patent Application (PCT) Number Hei 7-505445 (505,445/1995) teaches a nickel-free phosphate treatment method in order to solve the problems referenced above. This treatment method involves formation of a nickel-free phosphate coating by treatment with a phosphate conversion bath containing 0.2 to 2 g/L zinc ion, 0.5 to 25 mg/L copper ion, and 5 to 30 g/L phosphate ion. This method uses copper as a substitute metal for nickel, but still suffers from several problems. Since the allowable copper level in this conversion treatment bath is a very low 0.5 to 25 mg/L, management of the copper concentration in real-world lines is exceedingly difficult. Another concern is with electrolytic corrosion of the apparatus (equipment) caused by copper plating.

(0006)

Given this background, the development is desired of a phosphate conversion treatment method that does not use nickel but which nevertheless affords a post-painting adherence and post-painting corrosion resistance that are the equal of those afforded by existing phosphate conversion treatments that use nickel.

(0007)

(Problems to Be Solved by the Invention)

This invention was pursued in order to solve the problems in the prior art associated with removal of the nickel from phosphate treatment. The object of this invention is to provide a phosphate conversion treatment method that treats metal surfaces with a nickel-free conversion treatment bath and produces a phosphate conversion coating that evidences an excellent post-painting corrosion resistance and excellent paint adherence.

(0008)

(Means Solving the Problems)

The inventors carried out extensive investigations into means that would solve the problems caused by the removal of nickel from phosphate treatments. As a result, the inventors discovered that execution of phosphate conversion treatment after a special surface conditioning treatment of the metal enables elimination of the nickel ion from the conversion treatment bath while still producing a post-painting corrosion resistance and paint adherence equal to those of the prior art. This invention was achieved based on this discovery.

(0009)

More specifically, the first inventive method for the phosphate conversion treatment of metals characteristically comprises

contacting a metal with a surface conditioning bath that contains phosphate particles having a

diameter no greater than 5 μm and comprising at least 1 selection from phosphates that contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant

component, at least 1 selection from monosaccharides, polysaccharides, and derivatives thereof, and

contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

(0010)

The second conversion treatment method characteristically comprises

contacting a metal with a surface conditioning bath that contains phosphate particles having a diameter no greater than 5 μm and comprising at least 1 selection from phosphates that contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant component, at least 1 selection from orthophosphoric acid, polyphosphoric acids, and organophosphonic acid compounds, and

contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

(0011)

The third conversion treatment method characteristically comprises

contacting a metal with a surface conditioning bath that contains phosphate particles having a diameter no greater than 5 μm and comprising at least 1 selection from phosphates that contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant component, at least 1 water-soluble polymer compound selected from vinyl acetate polymers and derivatives thereof and the copolymers of vinyl acetate with monomer copolymerizable with vinyl acetate, and

contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

(0012)

The fourth conversion treatment method characteristically comprises contacting a metal with a surface conditioning bath that contains phosphate particles having a diameter no greater than 5 μm and comprising at least 1 selection from phosphates that contain at least 1 divalent and/or trivalent metal, and that contains, as accelerant component, at least 1 selection from the polymers and copolymers afforded by the polymerization of (a) at least 1 selection from monomers with chemical structure (1) and α,β-unsaturated carboxylic acid monomers and (b) no more than 50 weight% monomer copolymerizable with the aforesaid monomer (a)

(1) $H_2C{=}C(R^1){-}COOR^2$

(R^1 = H or CH_3, R^2 = H, C_1 to C_5 alkyl, or C_1 to C_5 hydroxyalkyl),

and contacting the resulting surface-conditioned metal with a nickel-free phosphate conversion treatment bath that contains 0.5 to 5 g/L zinc ion, 5 to 30 g/L phosphate ion, and conversion accelerant.

(0013)

In a preferred embodiment, the above-specified conversion treatment baths also contain from 0.1 to 3.0 g/L of at least 1 metal ion selected from the group consisting of the magnesium ion, cobalt ion, manganese ion, calcium ion, tungstate ion, and strontium ion.

(0014)

(Embodiments of the Invention)

The features of this invention are explained in greater detail hereinbelow. While no particular limitations apply to the metal on which the inventive phosphate treatment method may be executed, this metal is preferably steel sheet, zinc-plated steel sheet, zinc alloy-plated steel sheet, magnesium alloy, or aluminum alloy.

(0015)

It is necessary in the practice of the invention that the surface of the metal have been cleaned prior to the phosphate conversion treatment. Metal whose surface is already clean can be brought without further treatment into contact with the surface conditioning bath. However, in the case of treatment of metal whose surface is contaminated with adherent materials such as iron particles, dust, and oil, the contaminants adhering on the surface must be removed by cleaning, for example, by cleaning with a water-based alkaline degreaser or an emulsion degreaser or by solvent degreasing. When a water-based cleaner is used, the cleaning bath remaining on the metal surface is preferably removed by the provision of, for example, a water rinse step after the cleaning step.

(0016)

The surface conditioning process of this invention will now be explained in greater depth.

The particles of divalent and/or trivalent metal phosphate present in the inventive surface conditioning bath must have a particle size or diameter no greater than 5 μm. Insolubles of larger size are undesirable because — depending on the particular circumstances — they cannot be stably maintained in the aqueous bath. These phosphate particles not only function as

nuclei during phosphate crystal deposition, but also act to accelerate or promote the deposition reaction itself. More specifically, a portion of the divalent and/or trivalent metal phosphate particles adsorbed on the metal surface during the surface conditioning process undergoes dissolution in the phosphate conversion treatment bath and induces a substantial acceleration of the initial phosphate crystal deposition reactions by supplying one or more main components of the phosphate crystals to the region immediately adjacent to the metal surface.

(0017)

The divalent and trivalent metals used here are not critical, but preferably comprise at least 1 selection from Zn, Fe, Mn, Co, Ca, Mg, and Al. In order to function as nuclei during phosphate crystal deposition and accelerate the initial phosphate crystal deposition reactions, the divalent and/or trivalent metal phosphate particles are preferably present at a concentration from 0.001 to 30 g/L. Acceleration of the initial phosphate crystal deposition reactions cannot occur at a divalent and/or trivalent metal phosphate particle concentration below 0.001 g/L due to the small amount of divalent and/or trivalent metal phosphate particles that become adsorbed on the metal surface at such low concentrations. Concentrations below 0.001 g/L also prevent acceleration of the crystal deposition reactions due to the small number of divalent and/or trivalent metal phosphate particles available to act as crystal nuclei. Divalent and/or trivalent metal phosphate particle concentrations in excess of 30 g/L cannot be expected to provide additional promotion of the phosphate conversion reactions and hence will simply be uneconomical.

(0018)

The accelerant component that must be present in the inventive surface conditioning bath functions to improve the dispersion stability of the divalent and/or trivalent

metal phosphate particles and to accelerate adsorption of the divalent and/or trivalent metal phosphate particles onto the metal surface. More specifically, the accelerant component adsorbs to the surface of the divalent and/or trivalent metal phosphate particles and, through a steric hindrance activity and repulsive forces arising from its electrical charge, prevents collisions among the divalent and/or trivalent metal phosphate particles in the surface conditioning bath and thereby inhibits their aggregation and sedimentation. In addition, due to its structure the accelerant component itself has the ability to adsorb to metal surfaces and through this activity functions to accelerate adsorption to metal surfaces by the divalent and/or trivalent metal phosphate particles and thereby supports the appearance of the surface conditioning activity simply upon contact between the metal workpiece and surface conditioning bath.

(0019)

The accelerant component concentration is preferably from 1 to 2,000 ppm. At concentrations below 1 ppm a surface conditioning activity cannot be produced just by contact between the metal workpiece and the surface conditioning bath. Not only can no additional effects be expected at concentrations in excess of 2,000 ppm, but such concentrations result in an excessive adsorption by the polymer or copolymer on the surface of the metal workpiece and hence create the potential for impairing the phosphate conversion treatment.

(0020)

The accelerant component in the surface conditioning process in the first inventive phosphate conversion treatment method is at least 1 selection from monosaccharides, polysaccharides, and derivatives thereof. The basic structural saccharide of the monosaccharides, polysaccharides, and derivatives thereof used in the present invention can be selected from, for

example, fructose, tagatose, psicose, sorbose, erythrose, threose, ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, and talose.

(0021)

The use of the sodium and ammonium salts of said monosaccharides, polysaccharides, and derivatives thereof is also entirely unproblematic.

(0022)

The accelerant component in the surface conditioning process in the second inventive phosphate conversion treatment method is at least 1 selection from orthophosphoric acid, polyphosphoric acids, and organophosphonic acid compounds. Pyrophosphoric acid, triphosphoric acid, trimetaphosphoric acid, tetrametaphosphoric acid, hexametaphosphoric acid, and the sodium and ammonium salts of the preceding can be used for the polyphosphoric acid. Aminotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetramethylenephosphonic acid, diethylenetriaminepentamethylenephosphonic acid, and the sodium salts of the preceding can be used, for example, for the organophosphonic acid compound. The invention can use a single selection from the above-described orthophosphoric acid, polyphosphoric acids, and organophosphonic acid compounds or can use any combination thereof.

(0023)

The accelerant component in the surface conditioning process in the third inventive phosphate conversion treatment method is at least 1 water-soluble polymer compound selected from vinyl acetate polymers and derivatives thereof and copolymers of vinyl acetate and monomer copolymerizable with vinyl acetate. Usable by the present invention as the vinyl acetate polymer and derivatives thereof are the polyvinyl alcohols afforded by the saponification

of vinyl acetate polymers, the cyanoethylated polyvinyl alcohols afforded by the cyanoethylation of polyvinyl alcohol with acrylonitrile, the formalated polyvinyl alcohols afforded by the acetalation of polyvinyl alcohol with formaldehyde, the urethanized polyvinyl alcohols afforded by the urethanation of polyvinyl alcohol with urea, and the water-soluble polymer compounds afforded by the introduction of the carboxyl group, sulfonic group, or amide group into polyvinyl alcohol. The vinyl acetate-copolymerizable monomer usable by this invention can be exemplified by acrylic acid, crotonic acid, and maleic anhydride.

(0024)

The effects associated with the present invention will be fully manifested as long as the vinyl acetate polymer or derivative thereof or the copolymer of vinyl acetate and vinyl acetate-copolymerizable monomer is soluble in water. As a result, these effects are independent of the degree of polymerization and degree of functional group introduction of the subject polymers. The invention can use a single selection from the above-described polymers and copolymers or can use any combination thereof.

(0025)

The accelerant component in the surface conditioning process in the fourth inventive phosphate conversion treatment method is copolymer or polymer as afforded by the polymerization of (a) at least 1 selection from monomers with chemical structure (1) and α,β-unsaturated carboxylic acid monomers and (b) no more than 50 weight% monomer copolymerizable with the aforesaid monomer (a).

(0026)

(1) $H_2C{=}C(R^1){-}COOR^2$

(R^1 = H or CH_3, R^2 = H, C_1 to C_5 alkyl, or C_1 to C_5 hydroxyalkyl)

(0027)

The following are examples of usable monomer with chemical formula (1): methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, hydroxymethyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypentyl acrylate, hydroxymethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, and hydroxypentyl methacrylate.

(0028)

Usable as the α,β-unsaturated carboxylic acid monomer are, for example, acrylic acid, methacrylic acid, and maleic acid. Usable as monomer copolymerizable with the preceding monomers are, for example, vinyl acetate, styrene, vinyl chloride, and vinylsulfonic acid. The invention can use polymer synthesized by the polymerization of a single monomer from among the preceding or copolymer synthesized by the polymerization of any combination of the preceding monomers.

(0029)

The surface conditioning bath used by the inventive phosphate treatment methods can also contain an alkali metal salt or ammonium salt or a mixture thereof. The said alkali metal salt and ammonium salt are not critical as long as they take the form of at least 1 salt selected from the group consisting of orthophosphate salts, metaphosphate salts, orthosilicate salts, metasilicate salts, carbonate salts, bicarbonate salts, nitrate salts, nitrite salts, sulfate salts, borate salts, and organic acid salts. The invention can also use combinations of two or more selections from the aforesaid alkali metal and ammonium salts. The concentration of this component is not critical, but is preferably from 0.5 to 20 g/L.

(0030)

The phosphate conversion treatment process of this invention will now be considered in greater detail.

The phosphate conversion treatment bath used by this invention is an acidic aqueous solution that is essentially free of nickel ion and that contains zinc ion, phosphate ion, and accelerant. The zinc ion concentration in this phosphate conversion treatment bath is preferably from 0.5 to 5.0 g/L. A zinc ion concentration below 0.5 g/L, because it can prevent the formation of a coating of acceptable weight and can result in a diminished coverage ratio by the evolved phosphate crystals, can produce an inadequate post-painting corrosion resistance. A zinc ion concentration in excess of 5.0 g/L can cause a coarsening of the coating crystals, resulting in particular in a decline in the post-painting adherence.

(0031)

The phosphate ion concentration in the phosphate conversion treatment bath is preferably from 5.0 to 30 g/L. The use of a phosphate ion concentration below 5.0 g/L strongly impairs the production of a normal conversion coating. Concentrations in excess of 30.0 g/L are uneconomical since they provide no additional effect. The phosphate ion can be supplied by the addition of phosphoric acid or its aqueous solution to the phosphate conversion treatment bath or by the dissolution of, for example, sodium, magnesium, or zinc phosphate in the phosphate conversion treatment bath.

(0032)

The conversion treatment bath also contains an oxidizer known as a conversion accelerant. The conversion accelerant used in the phosphate conversion treatment process of this invention should be a substance that through its oxidizing activity has the ability to cause the

production of water from the electrons supplied from the metal workpiece surface and hydrogen ion at the cathode regions produced during etching. In other words, this should be a substance that acts to restrain hydrogen production during etching (depolarization activity). Otherwise, however, no particular limitations apply to the conversion accelerant.

(0033)

The phosphate conversion treatment bath of this invention can also contain from 0.1 to 3.0 g/L of at least 1 metal ion or metal oxide ion selected from the group consisting of the magnesium ion, cobalt ion, manganese ion, calcium ion, tungstate ion, and strontium ion. The presence of this component in the phosphate conversion treatment bath, through its incorporation into the phosphate coating and through its precipitation in a form separate from the phosphate, provides additional performance enhancements in the post-painting corrosion resistance and post-painting adherence, respectively. The use of a metal (oxide) ion concentration below 0.1 g/L is meaningless since no improvements in painting performance can be expected at such concentrations. Metal (oxide) ion concentrations above 3.0 g/L are economically wasteful since no additional improvements in painting performance occur at such concentrations. Such high concentrations can also hinder deposition of the zinc phosphate that is the main component in the phosphate treatment.

(0034)

The source of the metal ion can be, for example, the oxide, hydroxide, carbonate, sulfate, nitrate, or phosphate of the particular metal. The source of the aforementioned metal oxide ion can be, for example, the sodium or potassium salt.

(0035)

This metal (oxide) ion component can take the form of a single selection from the specified group or any combination of selections from said group.

(0036)

An etchant may be added to the phosphate conversion treatment bath in order to induce a uniform etch of the surface of the metal workpiece. Usable as this etchant are, for example, the fluoride ion and complex fluoride ions such as the fluosilicate ion. The fluorine compound used here can be, for example, hydrofluoric acid, fluosilicic acid, or a metal salt (sodium salt, potassium salt) of the preceding.

(0037)

The phosphate conversion treatment can be carried out by immersion or spraying or some combination thereof. Treatment for about 1 to 5 minutes can form a conversion coating satisfactorily robust for practical applications. The temperature of the phosphate conversion treatment bath is preferably from 30 to 60°C.

(0038)

The phosphate conversion treatment is preferably followed by a water rinse, and deionized water is preferably used in the final water rinse.

(0039)

The use of phosphate conversion coating technology as a paint undercoating requires the formation of a fine and dense phosphate conversion coating having the form of a thin film with a coating weight of 1.5 to 5 g/m^2. However, the required fine, dense, and thin phosphate conversion film essentially cannot be produced by execution of a nickel-free phosphate conversion treatment after the prior-art colloidal titanium surface conditioning

treatment. It is the surface conditioning process of this invention that is the prerequisite in this case for the production of fine, dense, and thin phosphate conversion films.

(0040)

(Examples)

Working and comparative examples of actual treatments are provided in the following in order to explain the advantageous effects of this invention in specific terms. The working examples that follow are simply examples of the application of the invention and in no way limit the applications of the invention or materials usable in the application of the invention.

(0041)

Materials tested

The following materials were treated in the working and comparative examples: electrogalvanized steel sheet (EG, sheet thickness = 0.8 mm, plating add-on = 20 g/m^2), galvannealed hot-dip galvanized steel sheet (GA, sheet thickness = 0.8 mm, plating add-on = 45 g/m^2), and cold-rolled steel sheet (CRS, sheet thickness = 0.8 mm, SPCC-SD).

(0042)

The treatment sequence common to the working and comparative examples was as follows.

(1) Degreasing with FINECLEANER L4460 (alkaline degreaser, registered trademark of Nihon Parkerizing Co., Ltd.), 20 g/L agent A, 12 g/L agent B, 43°C, 120 seconds, dipping

(2) Water rinse with tapwater: ambient temperature, 30 seconds, spray

(3) Surface conditioning

The conditions are described below in the tables for the working and comparative examples. The colloidal titanium surface conditioning treatments were run using Prepalene ZN, a product of Nihon Parkerizing Co., Ltd.

(4) Phosphate conversion treatment

The conditions are described below in the tables for the working and comparative examples. The treatment time was 120 seconds in all cases.

(5) Water rinse (tapwater): ambient temperature, 30 seconds, spray

(6) Deionized water rinse (deionized water with an electrical conductivity ≤ 0.2 μS/cm): ambient temperature, 20 seconds, spray

(7) Drain/dry: 120 seconds, hot wind at 90°C

(0043)

The following methods were used to test the painting performance of the test materials treated in the working and comparative examples.

(0044)

The coating appearance was evaluated on the following two-level scale:

+ : the coating was uniform

× : the coating exhibited a significant lack of uniformity with see-through.

(0045)

The test conditions and evaluation scale for the secondary (water-resistant) adherence were as follows. The tricoated sheet was immersed for 240 hours in a hot water bath (maintained at 40°C) that was being bubbled with air. The sheet was allowed to stand for 2 hours after removal from the hot water bath, after which time the peeling behavior was evaluated

by executing a grid cut (2 mm) in the sheet and subjecting this to tape peeling. The peeling behavior was evaluated using the following three-level scale.

++ : complete absence of peeling

+ : some peeling observed at the edges of the grid cut

× : substantial peeling

(0046)

The test conditions and evaluation scale for the hot saltwater immersion test were as follows. A cross cut was scribed with an acrylic cutter in the electrocoated monocoated sheet, and the specimen thus prepared was immersed for 240 hours in a 5 weight% saltwater bath that was maintained at 55°C and was bubbled with air. The specimen was allowed to stand for 1 hour after withdrawal from the saltwater bath, after which time the cross cut was peeled with tape and the width of peeling from the cut was evaluated. The peeling behavior was evaluated using the following three-level scale.

For the CRS:

++ : maximum peel width (both sides) less than 4 mm

+ : maximum peel width (both sides) at least 4 mm but less than 6 mm

× : maximum peel width (both sides) at least 6 mm

For the zinc plating:

++ : maximum peel width (one side) less than 3 mm

+ : maximum peel width (one side) at least 3 mm but less than 5 mm

× : maximum peel width (one side) at least 5 mm

(0047)

The test conditions and evaluation scale for salt spray testing were as follows. A cross cut was scribed with an acrylic cutter in the electrocoated monocoated sheet, and the specimen thus prepared was tested using a salt spray tester (5 weight% saltwater) maintained at 35°C. After the stipulated time (based on JIS Z-2371), the specimen was rinsed with water and the status of corrosion at the cross cut was evaluated using the following three-level scale.

For the CRS (salt spray test time = 960 hours):

++ : maximum rust width (both sides) less than 4 mm

+ : maximum rust width (both sides) at least 4 mm but less than 5 mm

× : maximum rust width (both sides) at least 5 mm

For the zinc plating (salt spray test time = 480 hours):

++ : maximum rust width (one side) less than 4 mm

+ : maximum rust width (one side) at least 4 mm but less than 5 mm

× : maximum rust width (one side) at least 5 mm

(0048)

Examples 1 to 25

The surface conditioning processes and phosphate treatment processes in Examples 1 to 25 are reported in Tables 1, 2, 7, 12, and 17.

(0049)

Comparative Examples 1 to 40

The surface conditioning processes and phosphate treatment processes in Comparative Examples 1 to 40 are reported in Tables 3, 4, 8, 9, 13, 14, 18, and 19.

(0050)

Tables 5, 6, 10, 11, 15, 16, 20, and 21 report the results for the conversion coating appearance and painting performance tests for the test materials treated in the working and comparative examples. The following abbreviations are used in the tables:

for the phosphate salt component:

Zn2FeP2 = $Zn_2Fe(PO_4)_2 \cdot 4H_2O$

Zn3P2 = $Zn_3(PO_4)_2 \cdot 4H_2O$

Zn2CaP2 = $Zn_2Ca(PO_4)_2 \cdot 4H_2O$

for the surfactant component:

EO11NPE = polyoxyethylene (EO : 11) nonylphenol ether

for the phosphorus compounds:

ATMPA = aminotrimethylenephosphonic acid

1-HEDPA = 1-hydroxyethylidene-1,1-diphosphonic acid

2-HEDPA = 2-hydroxyethylidene-1,1-diphosphonic acid

EDATMPA = ethylenediaminetetramethylenephosphonic acid.

(0051)

Table 1. Examples 1 to 5

			Example 1	Example 2	Example 3
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn2FeP2	Zn2FeP2
		particle size (μm)	0.5	0.5	0.5
		concentration (g/L)	1	1	1
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	glucose	glucose	glucose
		substituent(s)	CH_2COOH NO_2	CH_2COOH NO_2	CH_2COOH
		degree of substitution	≤ 1.8	≤ 1.8	0.7
		degree of polymerization	≤ 3,000	≤ 3,000	≤ 100
		concentration (ppm)	5	1,000	10
	alkali salt	designation	—	—	$NaNO_2$
		concentration (g/L)	—	—	0.5
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	10	15	20
		Zn^{2+}	0.8	1.3	2.2
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	1.0	—
		Mn^{2+}	0.5	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.3	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 1 is continued on the next page)

Table 1. Examples 1 to 5 (Continued from the previous page)

			Example 4	Example 5
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn2FeP2
		particle size (μm)	0.5	0.5
		concentration (g/L)	1	1
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	glucose	fructose
		substituent(s)	—	—
		degree of substitution	—	0
		degree of polymerization	1	≤ 100
		concentration (ppm)	2,000	2,000
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	—
		concentration (g/L)		—
	surfactant	abbreviation	—	—
		concentration (g/L)	—	—
	surface conditioning bath temperature (°C)		20	20
	surface conditioning treatment time (sec)		30	30
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	—	—
		Ca^{2+}	1.5	—
		Sr^{2+}	—	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	0.01
		NH_3OH^+	3.0	—
	conversion treatment temperature (°C)		35	43
	conversion treatment time (sec)		120	120

(0052)

Table 2. Examples 6 to 10

			Example 6	Example 7	Example 8
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (μm)	0.5	0.6	1.2
		concentration (g/L)	1	1	1
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	glucose xylose galactose	glucose	glucose
		substituent(s)	—	CH_2COOH	CH_2COOH CH_3
		degree of substitution	0	≥ 2	1.9
		degree of polymerization	≤ 500	≤ 200	≤ 1,000
		concentration (ppm)	100	100	1
	alkali salt	designation	—	—	$Na_2O{\cdot}SiO_2{\cdot}5H_2O$
		concentration (g/L)	—	—	5
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	11	15	22
		Zn^{2+}	0.9	1.3	2.0
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	—	—
		Mn^{2+}	0.6	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.9	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		38	43	49
	conversion treatment time (sec)		120	120	120

(Table 2 is continued on the next page)

Table 2. Examples 6 to 10 (Continued from the previous page)

			Example 9	Example 10
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn2CaP2
		particle size (μm)	0.4	0.4
		concentration (g/L)	10	5
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	glucose	fructose
		substituent(s)	CH_2COOH	—
		degree of substitution	1.0	0
		degree of polymerization	≤ 2,000	≤ 500
		concentration (ppm)	10	5
	alkali salt	designation	Na_2CO_3	$Na_3PO_4 \cdot 12H_2O$
		concentration (g/L)	1	10
	surfactant	abbreviation	—	EO11NPE
		concentration (g/L)	—	2.0
	surface conditioning bath temperature (°C)		20	40
	surface conditioning treatment time (sec)		30	120
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	—	—
		Ca^{2+}	1.0	—
		Sr^{2+}	—	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	—
		NH_3OH^+	3.0	3.5
	conversion treatment temperature (°C)		55	59
	conversion treatment time (sec)		120	120

(0053)

Table 3. Comparative Examples 1 to 5

			Comparative Example 1	Comparative Example 2	Comparative Example 3
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (μm)	0.5	0.6	1.2
		concentration (g/L)	1	1	1
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	glucose xylose galactose	glucose	glucose
		substituent(s)	—	CH_2COOH	CH_2COOH CH_3
		degree of substitution	0	≥ 2	1.9
		degree of polymerization	≤ 500	≤ 200	≤ 1,000
		concentration (ppm)	100	100	1
	alkali salt	designation	—	—	$Na_2O \cdot SiO_2 \cdot 5H_2O$
		concentration (g/L)	—	—	5
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	11	15	1.0
		Zn^{2+}	0.1	7.0	2.0
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	—	—
		Mn^{2+}	0.6	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.9	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		38	43	49
	conversion treatment time (sec)		120	120	120

(Table 3 is continued on the next page)

Table 3. Comparative Examples 1 to 5 (Continued from the previous page)

			Comparative Example 4	Comparative Example 5
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn2FeP2
		particle size (μm)	0.5	0.5
		concentration (g/L)	1	1
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	glucose	fructose
		substituent(s)	—	—
		degree of substitution	—	0
		degree of polymerization	1	≤ 100
		concentration (ppm)	2,000	2,000
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	—
		concentration (g/L)		—
	surfactant	abbreviation	—	—
		concentration (g/L)	—	—
	surface conditioning bath temperature (°C)		20	20
	surface conditioning treatment time (sec)		30	30
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	1.0	—
		Ca^{2+}	—	—
		Sr^{2+}	3.0	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	—
		NH_3OH^+	3.0	3.5
	conversion treatment temperature (°C)		55	20
	conversion treatment time (sec)		120	120

(0054)

Table 4. Comparative Examples 6 to 10

			Comparative Example 6	Comparative Example 7	Comparative Example 8
surface conditioning treatment process	PL-ZN concentration (g/L)		1	—	—
	phosphate particles	abbreviation	—	Zn3P2	Zn3P2
		particle size (μm)	—	0.6	6.5
		concentration (g/L)	—	1	1
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	—	—	glucose
		substituent(s)	—	—	CH_2COOH CH_3
		degree of substitution	—	—	1.9
		degree of polymerization	—	—	≤ 1,000
		concentration (ppm)	—	—	1
	alkali salt	designation	—	—	$Na_2O \cdot SiO_2 \cdot 5H_2O$
		concentration (g/L)	—	—	5
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	11	15	22
		Zn^{2+}	0.9	1.3	2.0
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	—	—
		Mn^{2+}	0.6	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.9	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 4 is continued on the next page)

Table 4. Comparative Examples 6 to 10 (Continued from the previous page)

			Comparative Example 9	Comparative Example 10
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn2FeP2
		particle size (μm)	0.4	0.5
		concentration (g/L)	10	0.00001
	monosaccharide, polysaccharide, or derivative thereof	basic structural saccharide	glucose	glucose
		substituent(s)	CH_2COOH	CH_2COOH
		degree of substitution	1.0	0.7
		degree of polymerization	≤ 2,000	≤ 100
		concentration (ppm)	5,000	10
	alkali salt	designation	Na_2CO_3	$NaNO_2$
		concentration (g/L)	1	0.5
	surfactant	abbreviation	—	—
		concentration (g/L)	—	—
	surface conditioning bath temperature (°C)		20	20
	surface conditioning treatment time (sec)		30	30
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	—	—
		Ca^{2+}	1.0	—
		Sr^{2+}	—	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	—
		NH_3OH^+	3.0	3.5
	conversion treatment temperature (°C)		39	43
	conversion treatment time (sec)		120	120

(0055)

Table 5. Appearance of the conversion coating and results of painting performance testing for Examples 1 through 10

	material tested	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
coating appearance	CRS	+	+	+	+	+	+	+	+	+	+
	EG	+	+	+	+	+	+	+	+	+	+
	GA	+	+	+	+	+	+	+	+	+	+
secondary (water-resistant) adherence	CRS	++	++	++	++	++	++	++	++	++	++
	EG	++	++	+	++	++	++	++	+	++	++
	GA	++	++	+	++	++	++	++	+	++	++
resistance to hot saltwater	CRS	++	++	++	++	+	++	+	++	++	+
	EG	++	++	++	++	++	++	+	++	++	++
	GA	++	++	++	++	++	++	+	++	++	++
resistance to salt spray	CRS	+	++	++	+	+	+	+	+	++	+
	EG	++	+	++	+	++	++	+	+	++	++
	GA	++	+	++	+	++	++	+	+	++	++

(0056)

Table 6. Appearance of the conversion coating and results of painting performance testing for Comparative Examples 1 through 10

	material tested	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10
coating appearance	CRS	×	+	×	×	×	+	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
secondary (water-resistant) adherence	CRS	++	+	++	++	++	+	++	++	++	+
	EG	×	×	×	×	×	×	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×
resistance to hot saltwater	CRS	×	++	×	×	×	++	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
resistance to salt spray	CRS	×	×	×	×	×	×	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×

(0057)

Table 7. Examples 11 to 15

			Example 11	Example 12	Example 13
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (μm)	0.5	0.5	1.7
		concentration (g/L)	5	1	1
	phosphorus compound				
	orthophosphoric acid and polyphosphoric acid	component	tripolyphosphoric acid	hexametaphosphoric acid	—
		concentration (ppm)	1	100	—
	organophosphonic acid	component	—	—	ATMPA
		concentration (ppm)	—	—	500
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	$Na_2O \cdot SiO_2 \cdot 5H_2O$	—
		concentration (g/L)	0.5	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	10	15	20
		Zn^{2+}	0.8	1.3	2.2
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	1.0	—
		Mn^{2+}	0.5	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.3	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 7 is continued on the next page)

Table 7. Examples 11 to 15 (Continued from the previous page)

				Example 14	Example 15
surface conditioning treatment process	PL-ZN concentration (g/L)			—	—
	phosphate particles	abbreviation		Zn2CaP2	Zn2FeP2
		particle size (μm)		0.6	0.5
		concentration (g/L)		5	10
	phosphorus compound				
	orthophosphoric acid and poly-phosphoric acid	component		—	—
		concentration (ppm)		—	—
	organophosphonic acid	component		1-HEDPA	EDATMPA
		concentration (ppm)		50	1,000
	alkali salt	designation		Na_2CO_3	$Na_3PO_4 \cdot 12H_2O$
		concentration (g/L)		5	10
	surfactant	abbreviation		—	EO11NPE
		concentration (g/L)		—	2.0
	surface conditioning bath temperature (°C)			20	40
	surface conditioning treatment time (sec)			30	120
phosphate conversion treatment process	component concentrations in g/L:				
			PO_4^{3-}	18	16
			Zn^{2+}	1.5	1.4
			Mg^{2+}	—	2.5
			Co^{2+}	—	—
			Mn^{2+}	—	—
			Ca^{2+}	1.5	—
			Sr^{2+}	—	0.9
			WO_4^{-2}	—	—
			NO_3^-	8.0	7.3
			F^-	—	0.1
			NO_2^-	—	0.01
			NH_3OH^+	3.0	—
	conversion treatment temperature (°C)			39	43
	conversion treatment time (sec)			120	120

(0058)

Table 8. Comparative Examples 11 to 15

			Comparative Example 11	Comparative Example 12	Comparative Example 13
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (μm)	0.5	0.5	1.7
		concentration (g/L)	5	1	1
	phosphorus compound				
	orthophosphoric acid and poly-phosphoric acid	component	tripolyphosphoric acid	hexametaphosphoric acid	—
		concentration (ppm)	1	100	—
	organophosphonic acid	component	—	—	ATMPA
		concentration (ppm)	—	—	500
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	NaOH	—
		concentration (g/L)	0.5	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	11	15	1.0
		Zn^{2+}	0.1	7.0	2.0
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	—	—
		Mn^{2+}	0.6	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.9	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 8 is continued on the next page)

Table 8. Comparative Examples 11 to 15 (Continued from the previous page)

				Comparative Example 14	Comparative Example 15
surface conditioning treatment process	PL-ZN concentration (g/L)			—	—
	phosphate particles	abbreviation		Zn2CaP2	Zn2FeP2
		particle size (μm)		0.6	0.5
		concentration (g/L)		5	10
	phosphorus compound				
	orthophosphoric acid and poly-phosphoric acid	component		—	—
		concentration (ppm)		—	—
	organophosphonic acid	component		2-HEDPA	EDATMPA
		concentration (ppm)		50	1,000
	alkali salt	designation		Na_2CO_3	$Na_3PO_4\cdot 12H_2O$
		concentration (g/L)		5	10
	surfactant	abbreviation		—	EO11NPE
		concentration (g/L)		—	2.0
	surface conditioning bath temperature (°C)			20	40
	surface conditioning treatment time (sec)			30	120
phosphate conversion treatment process	component concentrations in g/L:				
			PO_4^{3-}	18	16
			Zn^{2+}	1.5	1.4
			Mg^{2+}	—	2.5
			Co^{2+}	—	—
			Mn^{2+}	1.0	—
			Ca^{2+}	—	—
			Sr^{2+}	3.0	0.9
			WO_4^{-2}	—	—
			NO_3^-	8.0	7.3
			F^-	—	0.1
			NO_2^-	—	—
			NH_3OH^+	3.0	3.5
	conversion treatment temperature (°C)			39	20
	conversion treatment time (sec)			120	120

(0059)

Table 9. Comparative Examples 16 to 20

				Comparative Example 16	Comparative Example 17	Comparative Example 18
surface conditioning treatment process	PL-ZN concentration		(g/L)	1	—	—
	phosphate particles	abbreviation		—	Zn3P2	Zn3P2
		particle size	(μm)	—	0.5	6.5
		concentration	(g/L)	—	1	1
	phosphorus compound					
	orthophosphoric acid and polyphosphoric acid	component		—	—	—
		concentration	(ppm)	—	—	—
	organophosphonic acid	component		—	—	ATMPA
		concentration	(ppm)	—	—	500
	alkali salt	designation		$MgSO_4 \cdot 7H_2O$	—	—
		concentration	(g/L)	0.5	—	—
	surfactant	abbreviation		—	—	—
		concentration	(g/L)	—	—	—
	surface conditioning bath temperature (°C)			20	20	20
	surface conditioning treatment time (sec)			30	30	30
phosphate conversion treatment process	component concentrations in g/L:					
			PO_4^{3-}	11	15	22
			Zn^{2+}	0.9	1.3	2.0
			Mg^{2+}	2.0	—	—
			Co^{2+}	—	—	—
			Mn^{2+}	0.6	—	1.0
			Ca^{2+}	—	—	—
			Sr^{2+}	—	—	—
			WO_4^{-2}	—	—	0.3
			NO_3^-	8.9	7.6	9.0
			F^-	0.1	—	0.1
			NO_2^-	0.01	—	0.01
			NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)			40	45	50
	conversion treatment time (sec)			120	120	120

(Table 9 is continued on the next page)

Table 9. Comparative Examples 16 to 20 (Continued from the previous page)

			Comparative Example 19	Comparative Example 20
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn2FeP2
		particle size (μm)	0.6	0.00001
		concentration (g/L)	5	10
	phosphorus compound			
	orthophosphoric acid and poly-phosphoric acid	component	hexameta-phosphoric acid	—
		concentration (ppm)	3,000	—
	organophos-phonic acid	component	—	EDATMPA
		concentration (ppm)	—	1,000
	alkali salt	designation	Na_2CO_3	$Na_2O \cdot SiO_2 \cdot 5H_2O$
		concentration (g/L)	5	1
	surfactant	abbreviation	—	EO11NPE
		concentration (g/L)	—	2.0
	surface conditioning bath temperature (°C)		20	40
	surface conditioning treatment time (sec)		30	120
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	—	—
		Ca^{2+}	1.0	—
		Sr^{2+}	—	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	—
		NH_3OH^+	3.0	3.5
	conversion treatment temperature (°C)		39	43
	conversion treatment time (sec)		120	120

(0060)

Table 10. Appearance of the conversion coating and results of painting performance testing for Examples 11 through 15

	material tested	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15
coating appearance	CRS	+	+	+	+	+
	EG	+	+	+	+	+
	GA	+	+	+	+	+
secondary (water-resistant) adherence	CRS	++	++	++	++	++
	EG	++	++	+	++	++
	GA	++	++	+	++	++
resistance to hot saltwater	CRS	++	++	++	++	+
	EG	++	++	++	++	++
	GA	++	++	++	++	++
resistance to salt spray	CRS	+	++	++	+	+
	EG	++	+	++	+	++
	GA	++	+	++	+	++

(0061)

Table 11. Appearance of the conversion coating and results of painting performance testing for Comparative Examples 11 through 20

	material tested	Comp. Ex. 11	Comp. Ex. 12	Comp. Ex. 13	Comp. Ex. 14	Comp. Ex. 15	Comp. Ex. 16	Comp. Ex. 17	Comp. Ex. 18	Comp. Ex. 19	Comp. Ex. 20
coating appearance	CRS	×	+	×	×	×	+	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
secondary (water-resistant) adherence	CRS	++	+	++	++	++	+	++	++	++	+
	EG	×	×	×	×	×	×	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×
resistance to hot saltwater	CRS	×	++	×	×	×	++	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
resistance to salt spray	CRS	×	×	×	×	×	×	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×

(0062)

Table 12. Examples 16 to 20

			Example 16	Example 17	Example 18
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (μm)	0.5	1.5	0.5
		concentration (g/L)	5	8	1
	water-soluble polymer compound (VA = vinyl acetate)				
	VA polymer or derivative thereof	designation	polyvinyl alcohol (PVAlc)	carboxyl-modified PVAlc	sulfonic acid-modified PVAlc
	copolymer of VA and VA-copolymerizable monomer	monomer designation	—	—	—
		monomer weight%	—	—	—
	total	concentration (ppm)	1	500	2,000
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	$Na_2O \cdot SiO_2 \cdot 5H_2O$	—
		concentration (g/L)	0.5	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	10	15	20
		Zn^{2+}	0.8	1.3	2.2
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	1.0	—
		Mn^{2+}	0.5	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.3	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 12 is continued on the next page)

Table 12. Examples 16 to 20 (Continued from the previous page)

			Example 19	Example 20
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn2FeP2
		particle size (μm)	1.6	0.3
		concentration (g/L)	5	10
	water-soluble polymer compound (VA = vinyl acetate)			
	VA polymer or derivative thereof	designation	—	—
	copolymer of VA and VA-copolymerizable monomer	monomer designation	maleic acid	crotonic acid
		monomer weight%	80	70
	total	concentration (ppm)	1,000	10
	alkali salt	designation	Na_2CO_3	$Na_3PO_4 \cdot 12H_2O$
		concentration (g/L)	5	10
	surfactant	abbreviation	—	EO11NPE
		concentration (g/L)	—	2.0
	surface conditioning bath temperature (°C)		20	40
	surface conditioning treatment time (sec)		30	120
phosphate conversion treatment process	component concentrations in g/L:			
	PO_4^{3-}		18	16
	Zn^{2+}		1.5	1.4
	Mg^{2+}		—	2.5
	Co^{2+}		—	—
	Mn^{2+}		—	—
	Ca^{2+}		1.5	—
	Sr^{2+}		—	0.9
	WO_4^{-2}		—	—
	NO_3^-		8.0	7.3
	F^-		—	0.1
	NO_2^-		—	0.01
	NH_3OH^+		3.0	—
	conversion treatment temperature (°C)		39	43
	conversion treatment time (sec)		120	120

(0063)

Table 13. Comparative Examples 21 to 25

			Comparative Example 21	Comparative Example 22	Comparative Example 23
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (µm)	0.5	0.5	0.5
		concentration (g/L)	5	1	1
	water-soluble polymer compound (VA = vinyl acetate)				
	VA polymer or derivative thereof	designation	polyvinyl alcohol (PVAlc)	carboxyl-modified PVAlc	sulfonic acid-modified PVAlc
	copolymer of VA and VA-copolymerizable monomer	monomer designation	—	—	—
		monomer weight%	—	—	—
	total	concentration (ppm)	1	500	2,000
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	$Na_2O \cdot SiO_2 \cdot 5H_2O$	—
		concentration (g/L)	0.5	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	11	15	1.0
		Zn^{2+}	0.1	7.0	2.0
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	—	—
		Mn^{2+}	0.6	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.9	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 13 is continued on the next page)

Table 13. Comparative Examples 21 to 25 (Continued from the previous page)

			Comparative Example 24	Comparative Example 25
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn3P2
		particle size (μm)	1.6	0.5
		concentration (g/L)	5	1
	water-soluble polymer compound (VA = vinyl acetate)			
	VA polymer or derivative thereof	designation	—	—
	copolymer of VA and VA-copolymerizable monomer	monomer designation	maleic acid	crotonic acid
		monomer weight%	80	70
	total	concentration (ppm)	1,000	10
	alkali salt	designation	Na_2CO_3	$Na_3PO_4 \cdot 12H_2O$
		concentration (g/L)	5	10
	surfactant	abbreviation	—	EO11NPE
		concentration (g/L)	—	2.0
	surface conditioning bath temperature (°C)		20	40
	surface conditioning treatment time (sec)		30	120
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	1.0	—
		Ca^{2+}	—	—
		Sr^{2+}	3.0	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	—
		NH_3OH^+	3.0	3.5
	conversion treatment temperature (°C)		39	20
	conversion treatment time (sec)		120	120

(0064)

Table 14. Comparative Examples 26 to 30

			Comparative Example 26	Comparative Example 27	Comparative Example 28
surface conditioning treatment process	PL-ZN concentration (g/L)		1	—	—
	phosphate particles	abbreviation	—	Zn2FeP2	Zn3P2
		particle size (μm)	—	1.7	6.5
		concentration (g/L)	—	7	1
	water-soluble polymer compound (VA = vinyl acetate)				
	VA polymer or derivative thereof	designation	polyvinyl alcohol (PVAlc)	—	sulfonic acid-modified PVAlc
	copolymer of VA and VA-copolymerizable monomer	monomer designation	—	—	—
		monomer weight%	—	—	—
	total	concentration (ppm)	1	—	2,000
	alkali salt	designation	—	$Na_2O \cdot SiO_2 \cdot 5H_2O$	—
		concentration (g/L)	—	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	10	15	20
		Zn^{2+}	0.8	1.3	2.2
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	1.0	—
		Mn^{2+}	0.5	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.3	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 14 is continued on the next page)

Table 14. Comparative Examples 26 to 30 (Continued from the previous page)

			Comparative Example 29	Comparative Example 30
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn2FeP2
		particle size (μm)	1.6	0.3
		concentration (g/L)	5	0.00001
	water-soluble polymer compound (VA = vinyl acetate)			
	VA polymer or derivative thereof	designation	—	—
	copolymer of VA and VA-copolymerizable monomer	monomer designation	maleic acid	crotonic acid
		monomer weight%	80	70
	total	concentration (ppm)	3,000	10
	alkali salt	designation	Na_2CO_3	$Na_3PO_4{\cdot}12H_2O$
		concentration (g/L)	5	10
	surfactant	abbreviation	—	EO11NPE
		concentration (g/L)	—	2.0
	surface conditioning bath temperature (°C)		20	40
	surface conditioning treatment time (sec)		30	120
phosphate conversion treatment process	component concentrations in g/L:			
	PO_4^{3-}		18	16
	Zn^{2+}		1.5	1.4
	Mg^{2+}		—	2.5
	Co^{2+}		—	—
	Mn^{2+}		—	—
	Ca^{2+}		1.5	—
	Sr^{2+}		—	0.9
	WO_4^{-2}		—	—
	NO_3^-		8.0	7.3
	F^-		—	0.1
	NO_2^-		—	0.01
	NH_3OH^+		3.0	—
	conversion treatment temperature (°C)		39	43
	conversion treatment time (sec)		120	120

(0065)

Table 15. Appearance of the conversion coating and results of painting performance testing for Examples 16 through 20

	material tested	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20
coating appearance	CRS	+	+	+	+	+
	EG	+	+	+	+	+
	GA	+	+	+	+	+
secondary (water-resistant) adherence	CRS	++	++	++	++	++
	EG	++	++	+	++	++
	GA	++	++	+	++	++
resistance to hot saltwater	CRS	++	++	++	++	+
	EG	++	++	++	++	++
	GA	++	++	++	++	++
resistance to salt spray	CRS	+	++	++	+	+
	EG	++	+	++	+	++
	GA	++	+	++	+	++

(0066)

Table 16. Appearance of the conversion coating and results of painting performance testing for Comparative Examples 21 through 30

	material tested	Comp. Ex. 21	Comp. Ex. 22	Comp. Ex. 23	Comp. Ex. 24	Comp. Ex. 25	Comp. Ex. 26	Comp. Ex. 27	Comp. Ex. 28	Comp. Ex. 29	Comp. Ex. 30
coating appearance	CRS	×	+	×	×	×	+	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
secondary (water-resistant) adherence	CRS	++	+	++	++	++	+	++	++	++	+
	EG	×	×	×	×	×	×	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×
resistance to hot saltwater	CRS	×	++	×	×	×	++	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
resistance to salt spray	CRS	×	×	×	×	×	×	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×

(0067)

Table 17. Examples 21 to 25

			Example 21	Example 22	Example 23
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (μm)	0.5	0.5	1.7
		concentration (g/L)	5	1	1
	monomer with formula (1)	R^1	H	—	—
		R^2	C_2H_4OH	—	—
		weight%	100	—	—
	α,β-unsaturated carboxylic acid monomer	component	—	maleic acid	acrylic acid
		weight%	—	80	100
	copolymerizable monomer	component	—	vinyl acetate	—
		weight%	—	20	—
	copolymer	concentration (ppm)	1	500	2,000
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	$Na_2O \cdot SiO_2 \cdot 5H_2O$	—
		concentration (g/L)	0.5	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	10	15	20
		Zn^{2+}	0.8	1.3	2.2
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	1.0	—
		Mn^{2+}	0.5	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.3	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 17 is continued on the next page)

Table 17. Examples 21 to 25 (Continued from the previous page)

				Example 24	Example 25
surface conditioning treatment process	PL-ZN concentration (g/L)			—	—
	phosphate particles	abbreviation		Zn2CaP2	Zn2FeP2
		particle size (μm)		0.6	0.5
		concentration (g/L)		5	10
	monomer with formula (1)	R^1		CH_3	—
		R^2		C_3H_7OH	—
		weight%		20	—
	α,β-unsaturated carboxylic acid monomer	component		maleic acid	methacrylic acid
		weight%		80	50
	copolymerizable monomer	component		—	styrenesulfonic acid
		weight%		—	50
	copolymer	concentration (ppm)		1,500	5
	alkali salt	designation		KOH	$Na_3PO_4 \cdot 12H_2O$
		concentration (g/L)		5	10
	surfactant	abbreviation		—	EO11NPE
		concentration (g/L)		—	2.0
	surface conditioning bath temperature (°C)			20	40
	surface conditioning treatment time (sec)			30	120
phosphate conversion treatment process	component concentrations in g/L:		PO_4^{3-}	18	16
			Zn^{2+}	1.5	1.4
			Mg^{2+}	—	2.5
			Co^{2+}	—	—
			Mn^{2+}	—	—
			Ca^{2+}	1.5	—
			Sr^{2+}	—	0.9
			WO_4^{-2}	—	—
			NO_3^-	8.0	7.3
			F^-	—	0.1
			NO_2^-	—	0.01
			NH_3OH^+	3.0	—
	conversion treatment temperature (°C)			39	43
	conversion treatment time (sec)			120	120

(0068)

Table 18. Comparative Examples 31 to 35

			Comparative Example 31	Comparative Example 32	Comparative Example 33
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—	—
	phosphate particles	abbreviation	Zn2FeP2	Zn3P2	Zn3P2
		particle size (μm)	0.5	0.5	1.7
		concentration (g/L)	5	1	1
	monomer with formula (1)	R^1	H	—	—
		R^2	C_2H_4OH	—	—
		weight%	100	—	—
	α,β-unsaturated carboxylic acid monomer	component	—	maleic acid	acrylic acid
		weight%	—	80	100
	copolymerizable monomer	component	—	vinyl acetate	—
		weight%	—	20	—
	copolymer	concentration (ppm)	1	500	2,000
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	$Na_2O \cdot SiO_2 \cdot 5H_2O$	—
		concentration (g/L)	0.5	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	11	15	1.0
		Zn^{2+}	0.1	7.0	2.0
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	—	—
		Mn^{2+}	0.6	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.9	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 18 is continued on the next page)

Table 18. Comparative Examples 31 to 35 (Continued from the previous page)

			Comparative Example 34	Comparative Example 35
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn2FeP2
		particle size (μm)	0.6	0.5
		concentration (g/L)	5	10
	monomer with formula (1)	R^1	CH_3	—
		R^2	C_3H_7OH	—
		weight%	20	—
	α,β-unsaturated carboxylic acid monomer	component	maleic acid	methacrylic acid
		weight%	80	50
	copolymerizable monomer	component	—	styrenesulfonic acid
		weight%	—	50
	copolymer	concentration (ppm)	1,500	5
	alkali salt	designation	Na_2CO_3	$Na_3PO_4 \cdot 12H_2O$
		concentration (g/L)	5	10
	surfactant	abbreviation	—	EO11NPE
		concentration (g/L)	—	2.0
	surface conditioning bath temperature (°C)		20	40
	surface conditioning treatment time (sec)		30	120
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	1.0	—
		Ca^{2+}	—	—
		Sr^{2+}	3.0	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	—
		NH_3OH^+	3.0	3.5
	conversion treatment temperature (°C)		39	20
	conversion treatment time (sec)		120	120

(0069)

Table 19. Comparative Examples 36 to 40

			Comparative Example 36	Comparative Example 37	Comparative Example 38
surface conditioning treatment process	PL-ZN concentration (g/L)		1	—	—
	phosphate particles	abbreviation	—	Zn2CaP2	Zn3P2
		particle size (μm)	—	0.8	6.8
		concentration (g/L)	—	10	1
	monomer with formula (1)	R^1	H	—	—
		R^2	C_2H_4OH	—	—
		weight%	100	—	—
	α,β-unsaturated carboxylic acid monomer	component	—	—	acrylic acid
		weight%	—	—	100
	copolymerizable monomer	component	—	—	—
		weight%	—	—	—
	copolymer	concentration (ppm)	1	—	2,000
	alkali salt	designation	$MgSO_4 \cdot 7H_2O$	$Na_2O \cdot SiO_2 \cdot 5H_2O$	—
		concentration (g/L)	0.5	1	—
	surfactant	abbreviation	—	—	—
		concentration (g/L)	—	—	—
	surface conditioning bath temperature (°C)		20	20	20
	surface conditioning treatment time (sec)		30	30	30
phosphate conversion treatment process	component concentrations in g/L:				
		PO_4^{3-}	10	15	20
		Zn^{2+}	0.8	1.3	2.2
		Mg^{2+}	2.0	—	—
		Co^{2+}	—	1.0	—
		Mn^{2+}	0.5	—	1.0
		Ca^{2+}	—	—	—
		Sr^{2+}	—	—	—
		WO_4^{-2}	—	—	0.3
		NO_3^-	8.3	7.6	9.0
		F^-	0.1	—	0.1
		NO_2^-	0.01	—	0.01
		NH_3OH^+	—	1.5	—
	conversion treatment temperature (°C)		40	45	50
	conversion treatment time (sec)		120	120	120

(Table 19 is continued on the next page)

Table 19. Comparative Examples 36 to 40 (Continued from the previous page)

			Comparative Example 39	Comparative Example 40
surface conditioning treatment process	PL-ZN concentration (g/L)		—	—
	phosphate particles	abbreviation	Zn2CaP2	Zn2FeP2
		particle size (μm)	0.6	0.5
		concentration (g/L)	5	0.0001
	monomer with formula (1)	R^1	CH_3	—
		R^2	C_3H_7OH	—
		weight%	20	—
	α,β-unsaturated carboxylic acid monomer	component	maleic acid	methacrylic acid
		weight%	80	50
	copolymerizable monomer	component	—	styrenesulfonic acid
		weight%	—	50
	copolymer	concentration (ppm)	3,000	5
	alkali salt	designation	Na_2CO_3	$Na_3PO_4 \cdot 12H_2O$
		concentration (g/L)	5	10
	surfactant	abbreviation	—	EO11NPE
		concentration (g/L)	—	2.0
	surface conditioning bath temperature (°C)		20	40
	surface conditioning treatment time (sec)		30	120
phosphate conversion treatment process	component concentrations in g/L:			
		PO_4^{3-}	18	16
		Zn^{2+}	1.5	1.4
		Mg^{2+}	—	2.5
		Co^{2+}	—	—
		Mn^{2+}	—	—
		Ca^{2+}	1.5	—
		Sr^{2+}	—	0.9
		WO_4^{-2}	—	—
		NO_3^-	8.0	7.3
		F^-	—	0.1
		NO_2^-	—	0.01
		NH_3OH^+	3.0	—
	conversion treatment temperature (°C)		39	43
	conversion treatment time (sec)		120	120

(0070)

Table 20. Appearance of the conversion coating and results of painting performance testing for Examples 21 through 25

	material tested	Ex. 21	Ex. 22	Ex. 23	Ex. 24	Ex. 25
coating appearance	CRS	+	+	+	+	+
	EG	+	+	+	+	+
	GA	+	+	+	+	+
secondary (water-resistant) adherence	CRS	++	++	++	++	++
	EG	++	++	+	++	++
	GA	++	++	+	++	++
resistance to hot saltwater	CRS	++	++	++	++	+
	EG	++	++	++	++	++
	GA	++	++	++	++	++
resistance to salt spray	CRS	+	++	++	+	+
	EG	++	+	++	+	++
	GA	++	+	++	+	++

(0071)

Table 21. Appearance of the conversion coating and results of painting performance testing for Comparative Examples 31 through 40

	material tested	Comp. Ex. 31	Comp. Ex. 32	Comp. Ex. 33	Comp. Ex. 34	Comp. Ex. 35	Comp. Ex. 36	Comp. Ex. 37	Comp. Ex. 38	Comp. Ex. 39	Comp. Ex. 40
coating appearance	CRS	×	+	×	×	×	+	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
secondary (water-resistant) adherence	CRS	++	+	++	++	++	+	++	++	++	+
	EG	×	×	×	×	×	×	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×
resistance to hot saltwater	CRS	×	++	×	×	×	++	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
resistance to salt spray	CRS	×	×	×	×	×	×	×	×	×	×
	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×

(0072)

(Advantageous Effects of the Invention)

As has been described hereinabove, the inventive methods for the phosphate treatment of metals are highly advantageous in terms of environmental protection because they do not employ nickel. Moreover, these methods are also highly useful because they can produce entirely uniform, strongly paint-adherent, and highly post-painting corrosion-resistant phosphate coatings on a variety of metals, e.g., iron, steel, and zinc plating.

(Document Designation) Abstract

(Abstract)

(Problem)

To provide methods that produce high-quality phosphate coatings on metal surfaces and that do so using nickel ion-free phosphate coating-forming baths.

(Solution)

The metal is first brought into contact with a surface conditioning bath and is then brought into contact with a nickel ion-free phosphate coating-forming bath. The surface conditioning bath contains phosphate particles with a size no greater than 5 μm and also contains an accelerant component. The accelerant component can be a mono- or polysaccharide; or orthophosphoric acid, polyphosphoric acid, or an organophosphonic acid; or specific types of organic polymer compounds. In a preferred embodiment, the phosphate coating-forming bath contains 0.1 to 3.0 g/L metal ion selected from, for example, Mg, Co, Mn, and Ca.

(Selected Drawing(s)) None